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ADVANCED CALCIUM-THIONYL CHLORIDE HIGH-POWER BATTERY

Periodic Technical Report

by

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First Periodic Report

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<p>Recently we at TAU have made a breakthrough in the development of two advanced Ca-TC systems which have much better storage properties than the state-of-the-art Ca-SOCl₂ cell. This has been done by replacing the CaX₂ (X=AlCl₄) electrolyte by SrX₂ (type A), or BaX₂ (type B). The project's goals are to gain a better understanding of the electrochemistry of the advanced systems and to establish their safety and performance.</p> <p style="text-align: right;">Abstract cont.</p>					
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In this phase we improved significantly the cell performance. An improved C-size A7 type cell delivers 4.4 Ah at 0.9 A rate and room temperature which is 50% more than similar size commercial lithium cells have. The SAFT LSH14 lithium-thionyl chloride and the Duracell LO28SH lithium-SO₂ cells have at this rate only 2.9 and 2.7 Ah respectively. During one year of storage at room temperature the heat generation rate of 150 cm² C-size A7 type cells decreased to a level of 60-70 μ W. A cell lost 0.3 Ah after this storage period. The effect of several parameters on the corrosion rate of calcium in TC solutions was studied. Preliminary results indicate: SO₂ decreases corrosion, there is no stress corrosion due to twisting of Ca foils, the native oxide layer helps in preventing corrosion, Ca foils as received contain only about 90% metallic calcium. The role native calcium oxide layer plays depends on the type of electrolyte used.

Introduction

This project is a continuation of contract No. DAJA45-88-C-0012 (12/87-12/88). Its goals are to gain a better understanding of the electrochemistry of the advanced Ca/TC battery systems, which have been developed at TAU, and to establish their safety and performance.

Summary of the results of the first year

(contract DAJA45-88-C-0012)

This report contains four chapters. The calorimetric study of $\text{Ca}/\text{Sr}(\text{AlCl}_4)_2\text{-SOCl}_2 + 7\%(\text{v/v})\text{SO}_2$ C-size cells during constant-temperature discharge is reported in Chapter 1. Fresh and stored (70°C for four weeks) cells were discharged inside a dedicated home-made calorimeter on two loads: 9.4Ω and 4Ω at 30 and 55°C . The heat flow (W_T) of the cells (thermal power) during discharge was measured as a function of discharge time. There was no significant difference between fresh and stored cells with respect to heat generation during discharge.

There was no loss in capacity during the four weeks of storage at 70°C .

The following components of W_T were calculated and plotted against discharge capacity: W_S -thermodynamic; W_p -polarization; W_c -chemical. W_p was found to be the largest component of W_T . The maximum corrosion rate (I_c) of the calcium anode during discharge and its minimum Faradaic efficiency (ϵ) were calculated from W_c on the assumption that anodic corrosion is the major component of W_c . At 30°C , ϵ was about 0.9 while at 55° it drops from 0.87 at 2 mAcm^{-2} to 0.84 at 4 mAcm^{-2} . At 30°C the value of ϵ , is similar to that of t_i of the SEI of the calcium, indicating a similar corrosion mechanism for the calcium anode (both under OCV conditions and under load).

Chapter 2 presents a calorimetric study of the baseline cell $\text{Ca}/\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2 + 7\%(\text{V/V})\text{SO}_2$. The thermal power generated by the Ca/CaX_2



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cells is similar to that of the Ca/SrX_2 cells at 30°C . However at 55°C , $I_{c,a}$ of the Ca/CaX_2 cells is much higher. Thus the faradaic efficiency of the Ca/CaX_2 cells is similar or lower than that of the Ca/SrX_2 cells.

Chapter 3 presents the performance, safety and storage properties of Ca/CaX_2 and Ca/SrX_2 cells.

The Ca/CaX_2 cell loses most of its capacity after 4 weeks of storage at 70°C . However, the Ca/SrX_2 cell loses only 0-15% of its capacity when discharged over the temperature range -30 to $+60^\circ\text{C}$ after being stored for 4 weeks at 70°C . Its voltage delay is 0-100 sec. at -20 and -30°C after such storage. It has no voltage delay at room temperature and above. Cells equipped with a glass separator and a vent may vent on forced discharge as a result of overheating. The Ca/SrX_2 cell may be made safe and vent-free with the use of a Tefzel separator.

Chapter 4 presents a summary of the results regarding the properties of $\text{MX}_2\text{-SO}_2\text{-TC}$ solutions ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) including Raman spectra, viscosity and conductivity data. We explain the effect of SO_2 and temperature on the conductivity and conduction mechanism.

Preliminary performance of an improved C-size cell (type A7)

In the previous reports we predicted that the Ca/TC cell will have 25-50% more capacity than a similar size Li-SO_2 cell has. In this research phase we achieved this prediction. We reduced the thickness of the anode from 0.5 to 0.4mm and that of the cathode from 0.7 to 0.5 mm. This way the electrode area rose from 150 to 200-220 cm^2 . The separator is 60% porous 50μ thick Tefzel foil (Scimat). The electrolyte is 0.84M $\text{Sr}(\text{AlCl}_4)_2\text{-TC}$ with either 7 or about 20% (v/v) SO_2 . We have built 10 cells 5 with 7% SO_2 (type A7) and 5 with about 20% SO_2 (type A20). Four cells were discharged, two at RT and two at 30°C inside a calorimeter which has been described in the previous report.

The results are summarized in Table 1 and in Figs. 1 to 4.

Comparing the performance of the 150cm² cells to that of the 200cm² cells we can see the following:

At constant temperature discharge (30°C) and on 4Ω load the capacity increased from 2.2 Ah to 3.55-3.7 Ah and the average discharge voltage also increased by 50mV. The heat generation rate (thermal power) of the cells was not affected.

At RT on 3Ω load (0.8-0.9A) discharge, capacity rose from 3.2 Ah to 4.4 Ah. The maximum can's temperature decreased from 67 to about 50°C. The increase of SO₂ concentration from 7 to about 20% (v/v) does not seem to affect the capacity and cells' heating under these discharge conditions. However there is about 50mV loss in the average discharge voltage. This was previously found by B. Staniewicz et.al [33rd IPSS P.144 (1988)].

Table 2 shows the performance comparison of our improved C-size A7 type cell to two commercial systems. At about 0.9A room temperature discharge our Ca/TC A7 type cell delivers over 50% more capacity than have either the Li/TC LSH14 SAFT cell or Li/SO₂ LO28SH Duracell cell.

On the basis of these results it is expected that a D size Ca/TC cell of our technology will deliver about 10 Ah at 2A rate at RT.

Calcium purity problem

The purity of Pfizer bulk calcium is higher than 99.8%. However when it is rolled down to a thin foil it is contaminated by its oxide. Calcium foils as received contain only about 90% metallic calcium and the rest is CaO. Our previous calcium foils have been produced and rolled by Pfizer inside a glove box. However we run out of these batches and cells of (S₁₇-S₂₁) and T batches were assembled from calcium foils which were rolled down to 0.4mm in a regular room. The main difference between the previous calcium batches and the

present one is that previously most of the CaO was on the surface of the Ca foil while in the case of the last batch (rolled outside glove box) most of the CaO seems to be embedded in the bulk of the calcium. The question is to what extent this difference will affect the electrochemistry of the calcium and the characteristics of the cell.

Cell storage for a year at RT

Cells P-9 and P-4 have been stored at room temperature for over one year. Their heat output and OCV were measured at 20°C (Figs. 5 and 6). The OCV decreased from about 3.0V to 2.9V after 100 days and rose again to about 3.2V after 400 days. The heat output continuously decreased from about 800 μ w for fresh cells to about 60-70 μ w after 400 days. From the integral on the heat output it can be calculated that the capacity loss in one year was smaller than 0.5 Ah. Most of it 0.4 Ah was lost in the first 4 months. Cell P-4 was discharged at RT on 55 Ω load and yielded 3.7 Ah. A fresh cell of this batch yielded 4 Ah at the same rate of discharge.

Calcium corrosion tests - preliminary results

The goal of this set of experiments was to study the effect of SO₂ concentration, mechanical stress, type of calcium and paper sanding of the surface of the calcium, on the corrosion rate. The calcium strips were sealed in glass ampoules containing 0.84m Sr(AlCl₄)₂-TC-SO₂ solutions. These ampoules were stored for 28 days at 70°C. After this storage period, part of the calcium strips were taken for SEM tests and the other part was titrated to determine the content of the metal. Our preliminary findings are:

1. The calcium as received from the manufacturer contains only 92% metallic calcium and the rest is CaO.
2. The new batch, 0.4mm thick, which has been rolled in an uncontrolled

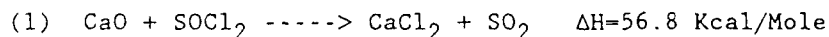
atmosphere contains a lot of CaO in the bulk of the metal.

3. Calcium that was sandpapered corrodes faster than calcium covered with a thick native oxide layer.
4. No stress corrosion was found. Calcium strips which were sandpapered and twisted a full two turns showed no higher corrosion than plain strips.
5. The corrosion rate of the "new" 0.4mm thick calcium is similar to that of the sandpapered "old" 0.5mm calcium, i.e. it is higher than that of the native oxide covered "old" calcium.
6. SO_2 affects the morphology of the passivating layer of calcium which is formed in TC solutions.
7. The corrosion rate decreases with the addition of SO_2 to the solutions. At 20% SO_2 it is about one half of that in SO_2 free solutions.

The influence of the native oxide layer on the characteristics of calcium electrodes.

The calcium metal foil (Pfizer, 99.8%) has a native oxide film 30-50 μ m when received from the manufacturer. Recently we became aware that this film plays a greater and more complex role than has been thought of before in determining the corrosion and performance characteristics of the calcium electrodes.

The CaO reaction with TC (1) is thermodynamically favored.



It was found that the rate of reaction (1) depends on the type of the metal ion (M) (M= Ca⁺⁺, Sr⁺⁺, Ba⁺⁺) in the thionyl-chloride (TC)/M(AlCl₄)₂ solution. Therefore we began a comprehensive study of the role of the oxide passive film on the behavior and properties of calcium electrodes.

In this study we use microcalorimetry, SEM + X-ray fluorescence analysis and AC technique to characterize untreated calcium electrodes and calcium electrodes from which the oxide layer was removed in several ways.

The following subjects are being investigated:

- a) The rate of exchange of the oxide layer to a chloride layer
- b) The rate of exchange of the Ca⁺⁺ in this layer with Sr⁺⁺ or Ba⁺⁺.
- c) The changes in the morphology of the film.
- d) The changes in the thickness and resistivity of the film as a result of the changes discussed in a), b) and c).
- e) The correlation between the nature of the film and the shelf-life of the calcium battery.

All the experiments are now in progress.

TABLE 1

Effect of Electrode Area on the Performance of a C-size Cell

Electrolyte: A7-0.84M $\text{Sr}(\text{AlCl}_4)_2^+$ 7% SO_2

Cell Code	Elect. area (cm^2)	Average Voltage (V)	Average Current (A)	Capacity 2V cut-off (Ah)	$W_{T,a}$ heat flow at 50% DOD (W)	Max. Temp. of can ($^{\circ}\text{C}$)
Q_{10}^*	150	2.3	0.58	2.2	1.1	-
S_{18}^*	200	2.35	0.59	3.7	1.1	-
T_2^*	220	2.35	0.59	3.55	1.1	-
P_1^{**}	150	2.8	0.93	3.2	-	67
S_{17}^{**}	200	2.65	0.88	4.4	-	49
T_{10}^{**+}	200	2.6	0.81	4.4	-	51

* Discharge inside the calorimeter at 30°C .

** RT discharge.

+ Electrolyte: 0.84 $\text{Sr}(\text{AlCl}_4)_2^+$ 20% SO_2 .

TABLE

Comparison of Performance of C-size Cells of Different Technologies at RT and 0.9A*

Technology	Cell Code	Ah	Average Voltage
Cd/TC (TAU)	Laboratory Prototype A7	4.4	2.65
Li/TC** (SAFT)	LSH14	2.9	3.2
Li/SO ₂ ** (Duracell)	10285H	2.7	2.7

* It is equivalent to at least 2A for D size cell.

** Information was taken from manufacturers' brochures.

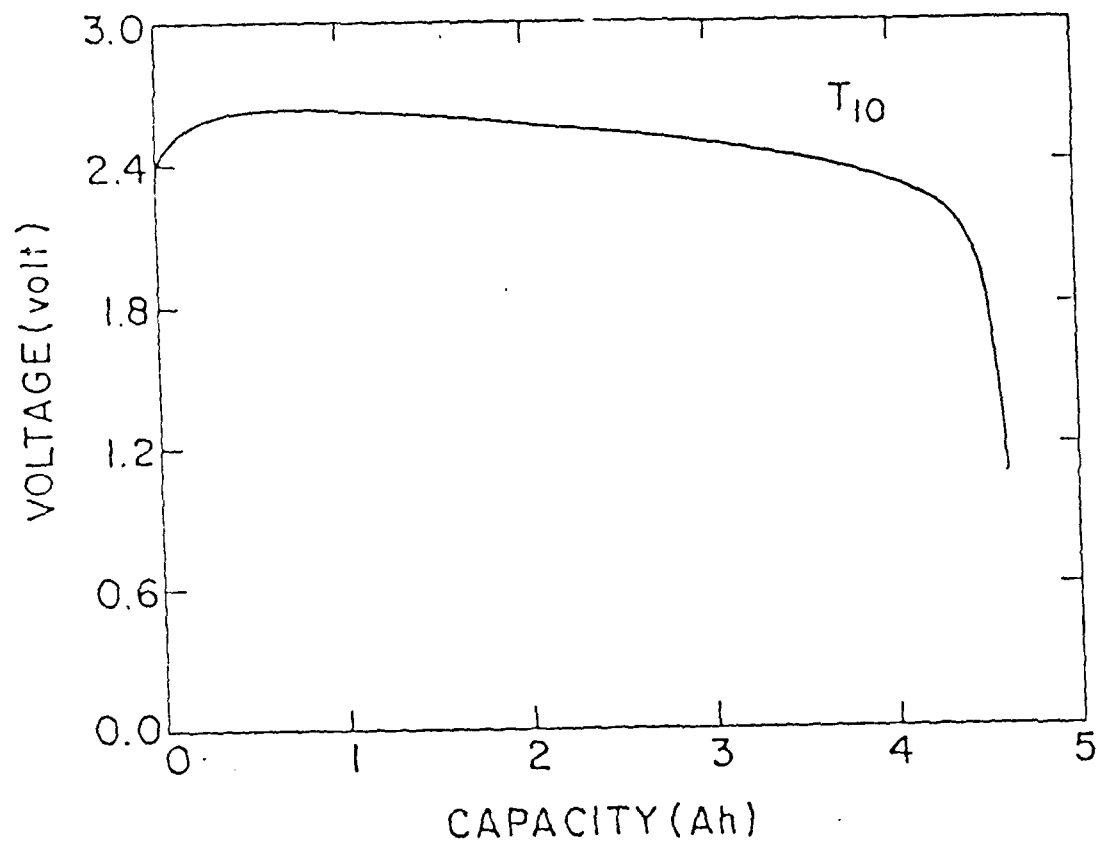


Fig. 1 Room temperature, discharge curve of C-size Ca/0.84M
SrX₂-TC + 20% (v/v) SO₂ cell (T₁₀), 200 cm², 3.2 Ω load.

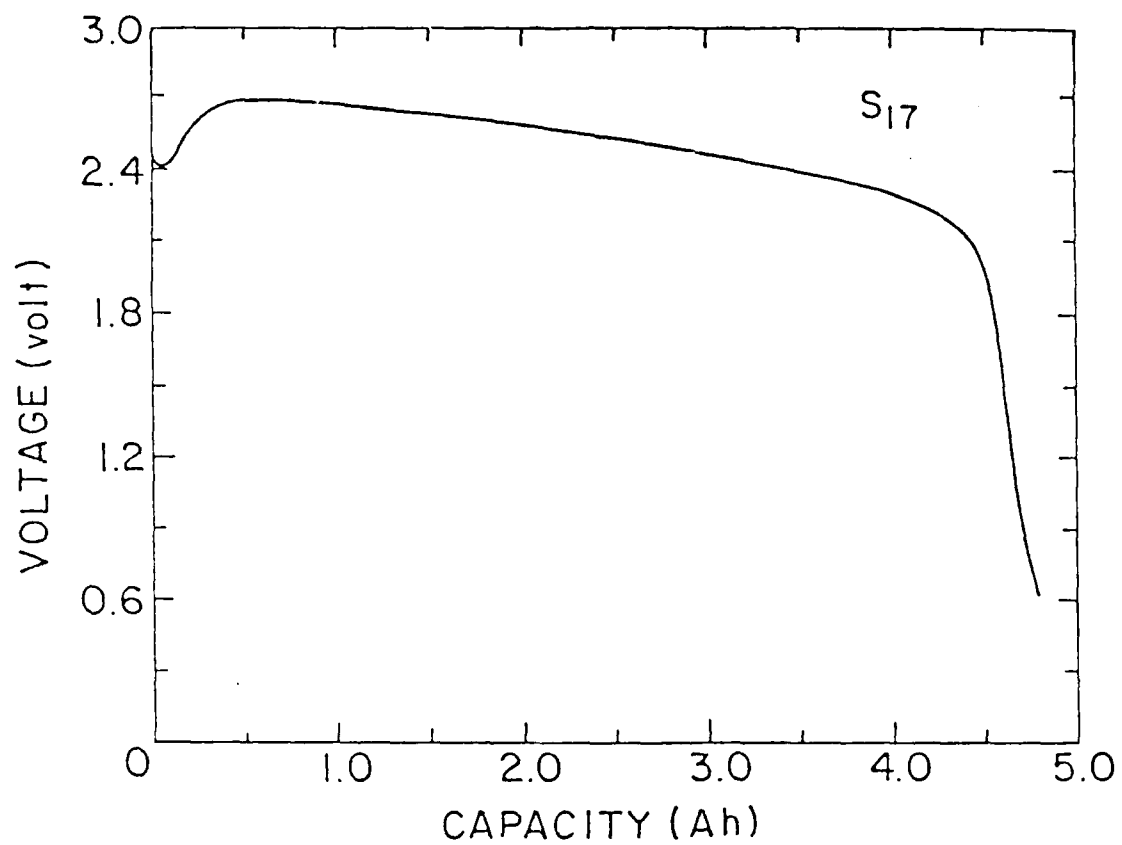


Fig. 2 Room temperature, discharge curve of C-size Ca/0.84M SrX₂-TC + 7% (v/v) SO₂ cell (S₁₇), 200 cm², 3.0 Ω load.

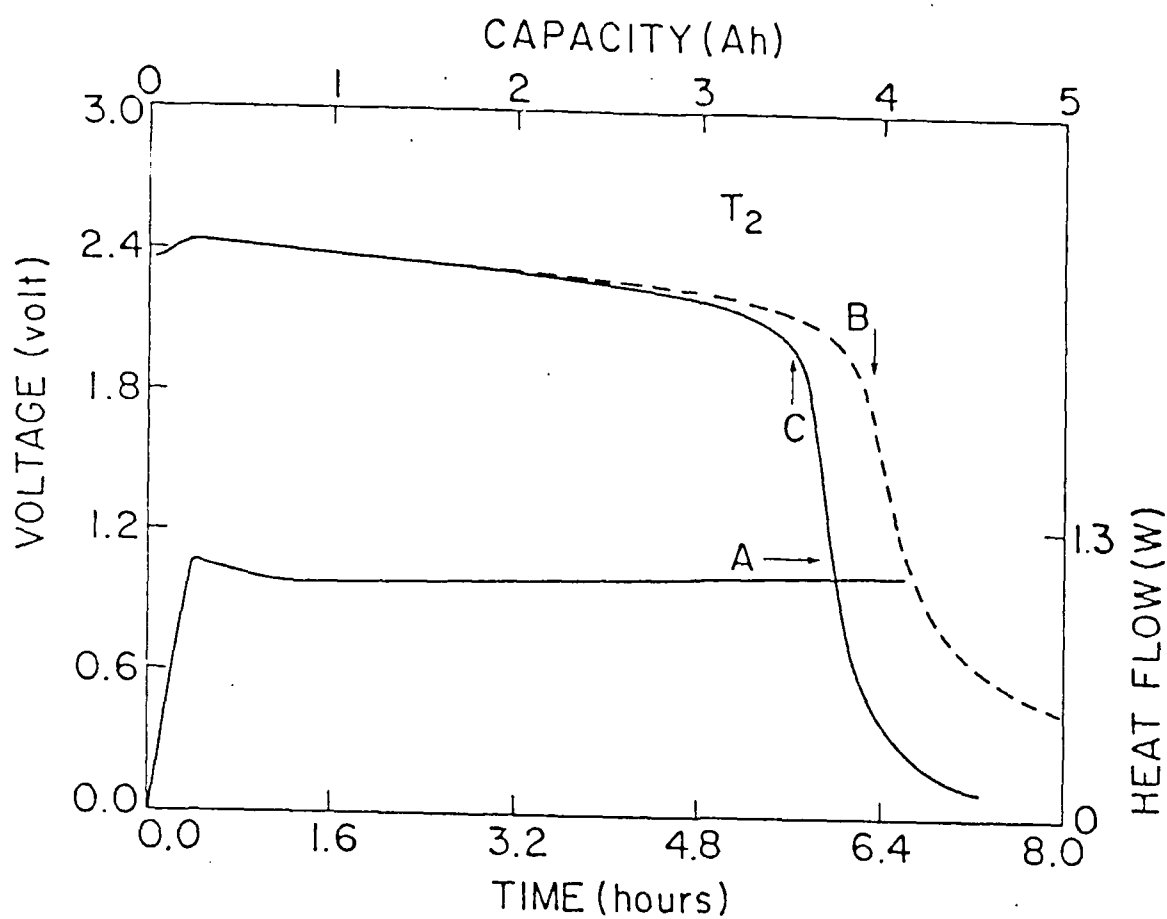


Fig. 3a Discharge (lines B and C) and calorimetric (line A) curves of C-size Ca/0.84M $\text{SrX}_2\text{-TC} + 7\%$ (v/v) SO_2 cell. T_2 fresh, 4.05Ω load, 30°C , 220 cm^2 .

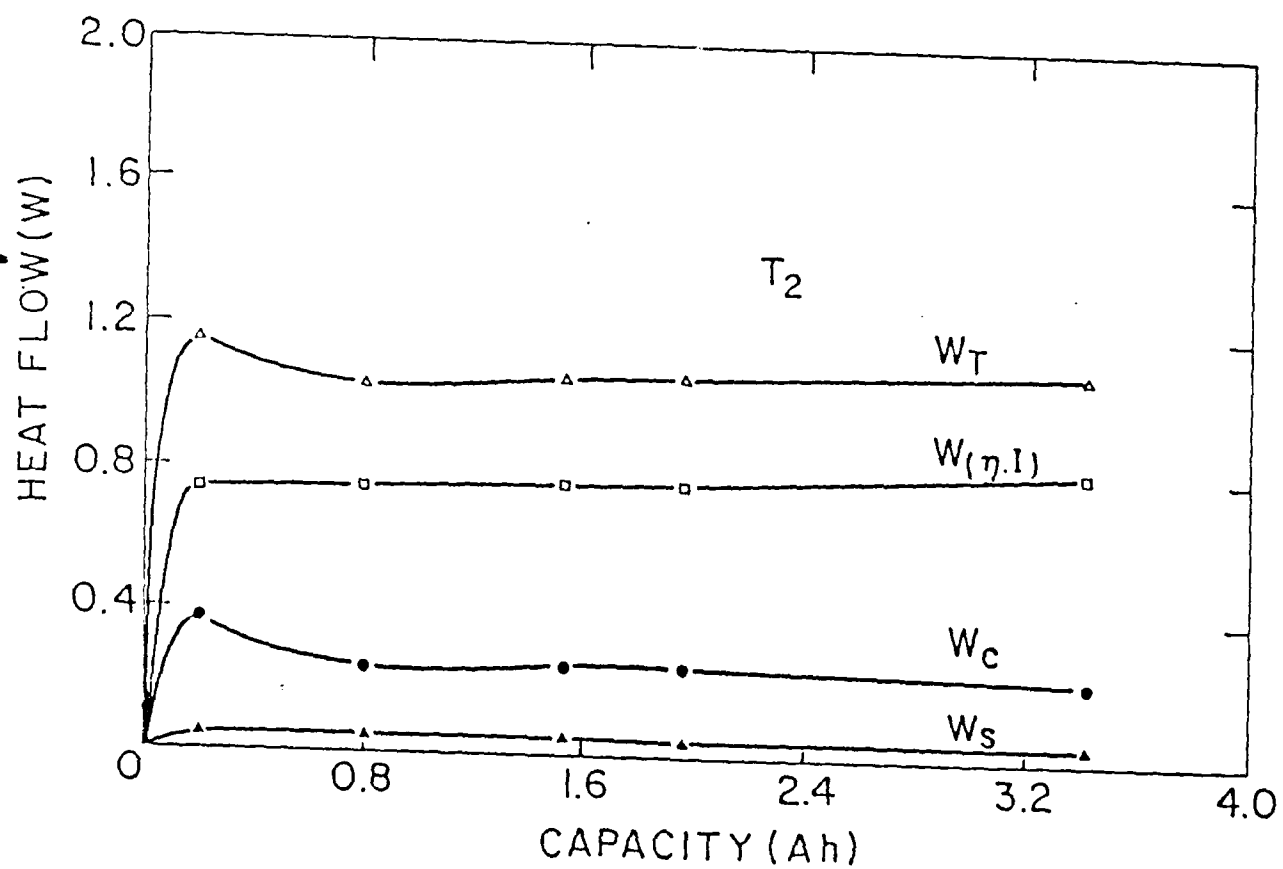


Fig. 3b Plots of W_T (total heat flow), W_p (polarization), W_c (chemical) and W_s (thermodynamic), for cell T_2 , vs. discharge capacity.

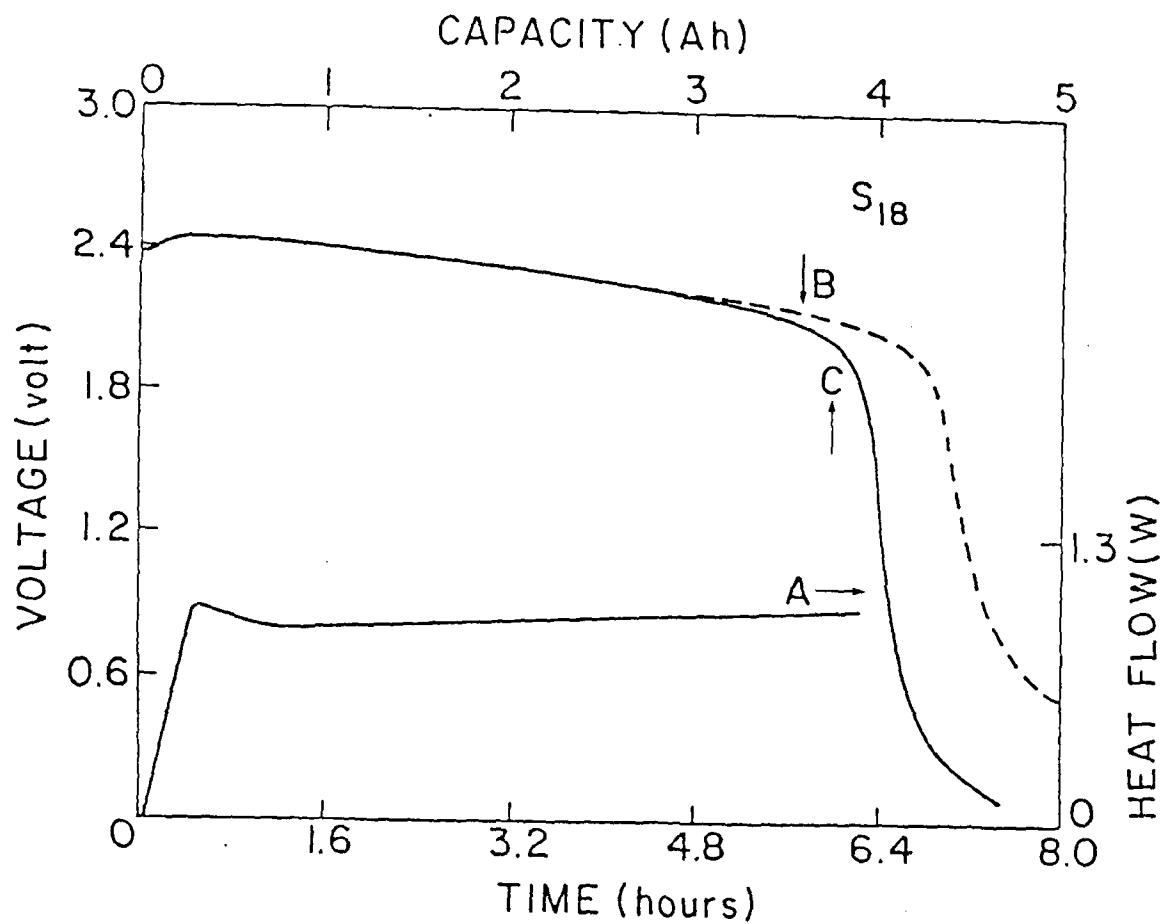


Fig. 4a Discharge (lines B and C) and calorimetric (line A) curves of C-size Ca/0.84M SrX₂-TC + 7% (v/v) SO₂ cell. S₁₈ fresh, 4.05 Ω load, 30°C, 200 cm².

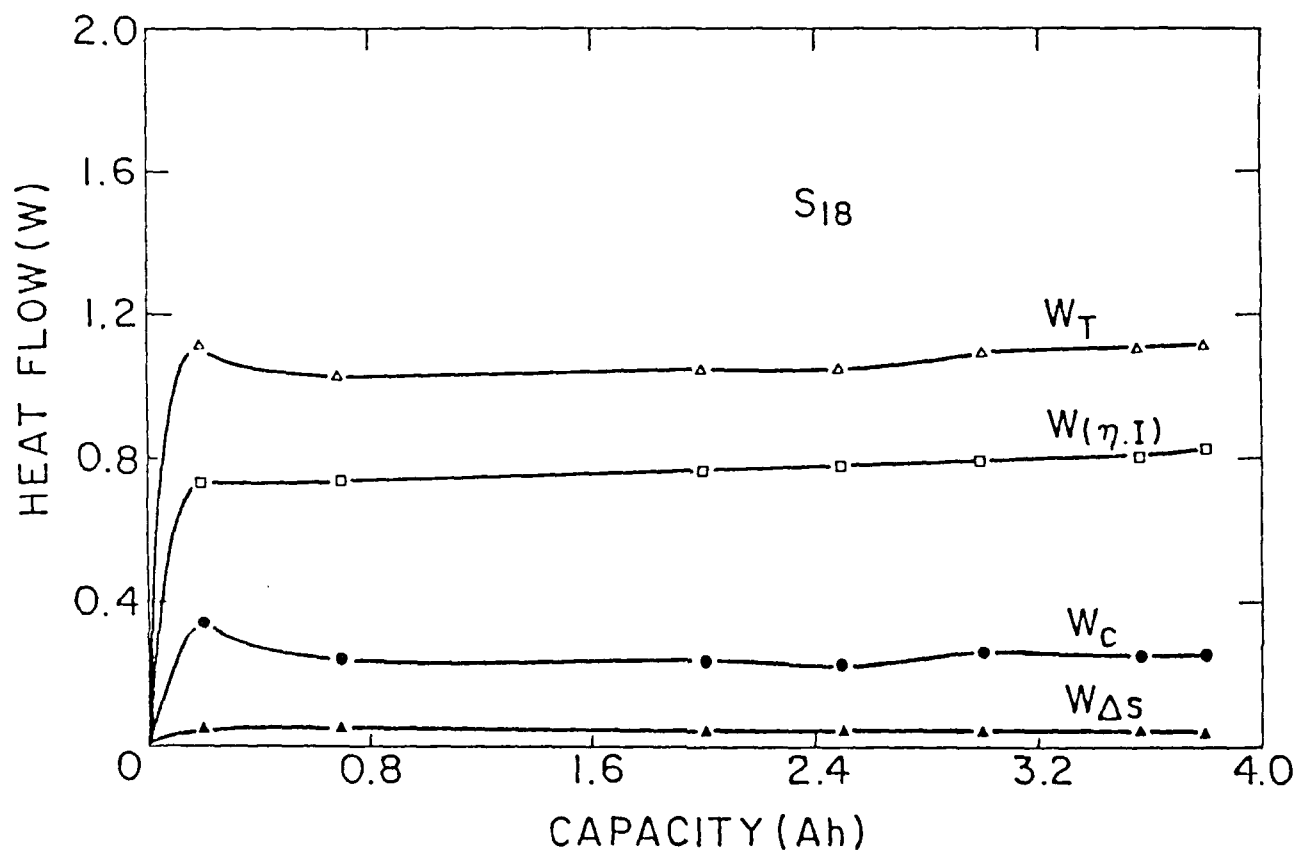


Fig. 4b Plots of W_T (total heat flow), W_p (polarization), W_c (chemical) and W_s (thermodynamic), for cell S_{18} , vs. discharge capacity.